OPTIMIZATION OF CARBON NANOTUBES FORMATION AND THE ROLE OF WATER VAPOR IN CATALYTIC DECOMPOSITION OF METHANE

By

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LIST OF ABBREVIATIONS

$Al(OH)_3$	Aluminium hydroxide
Al_2O_3	Aluminium oxide
ANOVA	Analysis of variance
Ar	Argon
C_2H_6	Ethane
C_3H_6	Propene
C_3H_8	Propane
C_4H_{10}	Butane
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3$	Calcium carbonate
CCVD	Catalytic chemical vapor deposition
CH_4	Methane
CNF	Carbon nanofiber
CNT	Carbon nanotube
Co	Cobalt
$Co(acac)_2$	Cobalt (II) acetylacetonate
$Co(NO_3)_2.6H_2O$	Cobalt (II) nitrate hexahydrate
CO	Carbon monoxide
CO_2	Carbon dioxide
Co_2AlO_4	Cobalt(II) aluminate
CoO	Cobalt oxide
Cr	Chromium
CRD	Completely randomized design
Cu	Copper
CuO	Copper oxide
CVD	Chemical vapor deposition
d	Diameter
DoE	Design of experiment
EAD	Electric arc discharge
EIA	Energy Information Administration
FBCVD	Fluidized bed chemical vapor deposition
Fe	Iron
$Fe(acac)_3$	Ferrous acetylacetonate
$Fe(NO_3)_3$	Iron(III) nitrate
Fe_2O_3	Iron(III) oxide
FI	Factor interaction
F-value	Fisher test value
$g_{(CoOx\text{-}MoOx)}$	Gram of bimetallic (cobalt oxide-molybdenum oxide)
GC	Gas chromatograph
g_c	Gram of deposited carbon
g_{cat}	Gram of catalyst
GHSV	Gas hourly space velocity
h	Hour
H	Height
H_2	Hydrogen

H_2S	Hydrogen sulphide
He	Helium
HRTEM	High resolution transmission electron microscopy
i-C_4H_{10}	Isobutane
ID	Inner diameter
L	Length
MCM-41	Mobil Catalytic Material Number 41
$Mg(OH)_2$	Magnesium hydroxide
$MgCO_3$	Magnesium carbonate
MgO	Magnesium oxide
min	Minute
ml	Milliliter
mm	Millimeter
Mn	Manganese
Mo	Molybdenum
MoO	Molybdenum oxide
MS	Molecular sieve
MWCNT	Multi-walled carbon nanotubes
N.A.	Not available
N_2	Nitrogen
n-C_4H_{10}	Butane-n
Ne	Neon
$(NH_4)_6Mo_7O_{24}.4H_2O$	Hexaammonium heptamolybdate tetrahydrate
Ni	Nickel
NiO	Nickel oxide
nm	Nanometer
O_2	Oxygen
OD	Outer diameter
OFAT	One factor at a time
Os	Osmium
Pd	Palladium
PEM	Proton-exchange membrane
ppm	Part per million
Prob	Probability
Pt	Platinum
Rh	Rhodium
RSM	Response surface methodology
Ru	Ruthenium
S/N	Signal to noise
sccm	Standard cubic centimeters per minute
SEI	Secondary electron imaging
SEM	Scanning electron microscopy
SiO_2	Silicon dioxide
SWCNT	Single-walled carbon nanotubes
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
TiO_2	Titanium dioxide
VLS	Vapor-liquid-solid
W	Wide

wt	Weight
Xe	Xenon
ZrO_2	Zirconium oxide

LIST OF SYMBOLS

A	Coded term of reaction temperature
2_{III}^{6-3}	2 level fractional with resolution III
Å	Ångstrom
B	Coded term of reaction time
C	Coded term of catalyst weight
D	Coded term of metal loading
E	Coded term of methane flow rate
F	Coded term of nitrogen flow rate
k	Design factor
x	Numerical value
γ	Gamma

PENGOPTIMUMAN PEMBENTUKAN NANOTIUB KARBON DAN PERANAN WAP AIR DALAM PENGURAIAN BERMANGKIN METANA

ABSTRAK

Nanotiub karbon (CNT) disintesis menggunakan mangkin CoO_x-MoO_x/Al_2O_3 melalui penguraian metana dalam sistem reaktor tiub kuarza mendatar. Untuk memastikan kajian proses dan proses pengoptimuman dijalankan dengan sistematik, penyelidikan ini dijalankan dengan menggunakan rekabentuk ujikaji statistik (DoE). Kesan enam pembolehubah proses (suhu tindak balas, masa tindak balas, jumlah mangkin, pemuatan logam, kadar aliran metana dan kadar aliran nitrogen) pada kadar hasil karbon dan nisbah I_D/I_G CNT yang dihasilkan adalah disiasat dengan menggunakan kaedah faktorial berperingkat peleraian III (FFD) berganding dengan metodologi permukaan sambutan (RSM), iaitu rekabentuk Box-Behnken (BBD). Suhu tindak balas, masa tindak balas dan pemuatan logam dikenalpastikan sebagai pembolehubah penentuan yang mempengaruhi hasil karbon dan nisbah I_D/I_G CNT, seperti yang dikenalpasti dengan menggunakan 2^{6-3}_{III} FFD; maklumat ini seterusnya digunakan untuk membina permukaan sambutan dengan mengguna BBD. Keadaan optimum diperolehi pada suhu tindak balas 762°C, masa tindak balas selama 2.3 jam dan 27% pemuatan logam, dengan kadar hasil karbon sebanyak 350% dan I_D/I_G bernilai 0.595. Kemudian, kesan wap air terhadap aktiviti mangkin dan hayat mangkin disiasat, berdasarkan analisis gas efluen. Kemasukan jumlah wap air yang bersesuaian, iaitu 133.3 ppm ke dalam ambien tindak balas didapati meningkatkan dan menampung aktiviti mangkin melalui proses punaran karbon amorfus yang menyalut permukaan tapak aktif, mengakibatkan penukaran metana dan hasil karbon

metana dan hasil karbon yang lebih tinggi. Aktiviti mangkin kekal selepas tindak balas selama 2 jam, dan kadar hasil karbon meningkat kepada 1076%. Tambahan pula, didapati bahawa CNT mempamerkan bentuk struktur dan morfologi yang lebih baik dan tanpa karbon amorfus yang melekat melalui cerapan gambar mikroskop elektron pancaran peleraian tinggi (HRTEM). Walau bagaimanapun, tumbuhbesaran CNT terbantut apabila wap air terlalu banyak. Bekalan wap air berterusan dengan jumlah yang bersesuaian adalah lebih baik untuk menghasilkan CNT yang mempunyai hablur yang lebih baik. Kajian ini diakhiri dengan demonstrasi penguraian gas asli untuk penghasilan CNT atas mangkin yang sama pada keadaan optimum. Hayat mangkin didapati lebih panjang berbanding penguraian metana, dan karbon berfilamen dihasilkan, ialah campuran CNT dan nanofiber karbon (CNFs). Penemuan ini mencadangkan satu kaedah alternatif dengan kos yang efisien untuk penghasilan bersama CNT, CNFs dan hidrogen tanpa menggunakan punca karbon berketulenan tinggi.

OPTIMIZATION OF CARBON NANOTUBES FORMATION AND THE ROLE OF WATER VAPOR IN CATALYTIC DECOMPOSITION OF METHANE

ABSTRACT

Carbon nanotubes (CNT) were synthesized over CoO_x-MoO_x/Al_2O_3 catalyst via decomposition of methane in a horizontal quartz tube reactor system. In order to have a systematic process study and process optimization, this research study was carried out by using statistical design of experiments (DoE). The effects of the six process variables (reaction temperature, reaction time, catalyst amount, metal loading, methane flow rate and nitrogen flow rate) on the carbon yield and the I_D/I_G ratio of as-produced CNT were investigated using Resolution III fractional factorial design (FFD) coupled with response surface methodology (RSM), i.e. Box-Behnken design (BBD). Reaction temperature, reaction time and metal loading were identified to be the decisive process variables influencing the carbon yield and the intensity radio of D-peak and G-peak in Raman spectra (I_D/I_G ratio), as distinguished using a 2_{III}^{6-3} FFD; then BBD was exploited to construct a response surface from the decisive process variables. The optimum parameter set was found at a reaction temperature of 762°C, 2.3 h reaction time and metal loading of 27%, with the carbon yield and I_D/I_G of 350% and 0.595, respectively. The effect of water vapor on catalytic activity and catalyst lifetime was investigated afterwards, based on analysis of the effluent gas. The introduction of an appropriate amount of water vapor, i.e. 133.3 ppm into the reaction ambient enhanced and sustained the catalytic activity by etching the amorphous carbon coated on active sites surface, led to higher methane conversion

and carbon yield as well. The catalytic activity was sustained after 2 h reaction and the carbon yield increased to 1076%. Furthermore, it was found that the CNT exhibited better structure and morphology without the adherence of amorphous carbon, as observed from HRTEM image. However, the CNT growth is suppressed when the water vapor was over supplied, due to the water induced oxidation of active sites. A continuous supply of controlled amount water vapor is preferable in order to produce CNT with higher crystallinity. This research work is ended with the demonstration of natural gas decomposition over the said catalyst at optimized conditions for the production of CNT. The catalyst lifetime was found longer compared to decomposition of methane, with the formation of filamentous carbon, i.e. a mixture of CNT and carbon nanofibers (CNFs). The findings suggest an alternative cost effectively route for co-producing CNT, CNFs and hydrogen without using high purity carbon source.

CHAPTER ONE:

INTRODUCTION

This chapter provides an overall introduction to the research project. Brief definition of nanotechnology and carbon nanotubes (CNT) is outlined at the beginning of this chapter. Apart from that, information of methane and natural gas used as feedstock in this study are given as well. Finally, this chapter concludes with problem statement, objectives and thesis organization of thesis content.

1.1 Nanotechnology

The general concept of nanotechnology has been discussed tentatively by scientists since the late nineteenth century. However, most scientists date the first specific reference to the classic take by American physicist Richard Feynman gave in 1959 at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech) (Feynman, 1960). The term nanotechnology was defined in the mid-1970s by a Japanese electrical engineer named Norio Taniguchi as follows: "'Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule." (Taniguchi, 1974). In the 1980s, the basic idea of this definition was explored in much more depth by the American engineer Eric Drexler in his 1986 best-seller *Engines of Creation: The Coming Era of Nanotechnology* (Drexler, 1986), promoted the technological significance of nano-scale phenomena and devices, and this book is considered the first book on the topic of nanotechnology .

Nanotechnology can be defined as the creation of functional materials, devices, and systems through the manipulation of matter on the nanometer (nm) length scale (less than 100 nm). In the case of nanotechnology, the prefix 'nano' signifies a billionth of a meter, or 10^{-9} of a meter. Therefore, nanotechnologies focus on the design, characterization, production, and application of nanoscale systems and components. Figure 1.1 presents a diagram showing the region that belongs to nanotechnology.

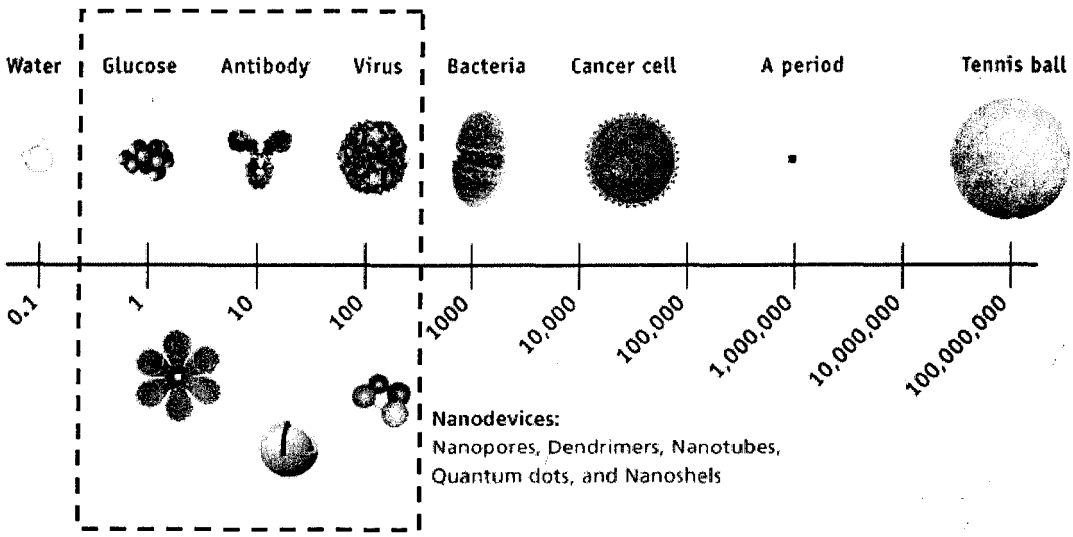

Figure 1.1. The diagram showing the nanotechnology region (FDA, 2010).

Nanotechnology is a multidisciplinary field encompassing biology, chemistry, physics and engineering. There are two main approaches used in nanotechnologies, namely "bottom- up" and "top- down" approaches. In the "bottom-up" approach, materials and devices are built from molecular components, which assemble themselves chemically by principles of molecular recognition. This level of control enables an unlimited creation of new materials and new devices. This approach is usually performed by using catalysts to induce chemical synthesis, or the bonding of

atoms and molecules to produce new materials. Meanwhile, in the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control. Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. One example is the increase in surface area to volume ratio alters mechanical, thermal and catalytic properties of materials.

Without any doubt, the 21st century will be a period of significant progress for nanotechnology. Between 1997 and 2005, the investment in nanotech research and development by governments around the world soared from $432 million to about $4.1 billion, and corresponding industry investment exceeded that of governments by 2005. By 2015, products incorporating nanotech will contribute approximately $1 trillion to the global economy (Roco, 2006). It is strongly believed that nanotechnology will complement and change life science, medicine technology, environmental technology, material science and so on to a new expanse in a near future.

1.2 The element carbon

1.2.1 Allotropes of carbon

Carbon, without any doubt is one of the most well known elements on Earth, as can be seen by the fact that it is the basis of life in this planet. Carbon has an electronic configuration of $1s^2\ 2s^2\ 2p^2$, in which the $2s^2\ 2p^2$ orbits are normally hybridized to form 4 degenerate orbitals (sp^3 hybridized atom). This enables the carbon atom to form 4 identical covalent bonds to other atoms. Common carbon

compounds in the environment include the gases carbon dioxide (CO_2) and methane (CH_4) (Cleveland, 2008).

Due to the different molecular configurations can be formed by carbon, it exists in several forms called allotropes. Before 1991, the known allotropes of carbon include diamond, graphite, fullerene and amorphous carbon. In 1991, Sumio Iijima from the NEC Laboratory in Tsukuba, Japan, discovered another form of carbon, which composed entirely of sp^2 bonds, similar to graphite. The discovered carbon was in the form of tubular and the centre core of the tubular carbon was hollow (Iijima, 1991). Due to the nano-size and hollow core of this tubular carbon structure, the name of "Carbon Nanotube (CNT)" was given. Since then, CNT attracted intense study from researchers all over the world. The allotropes of carbon are shown in Figure 1.2.

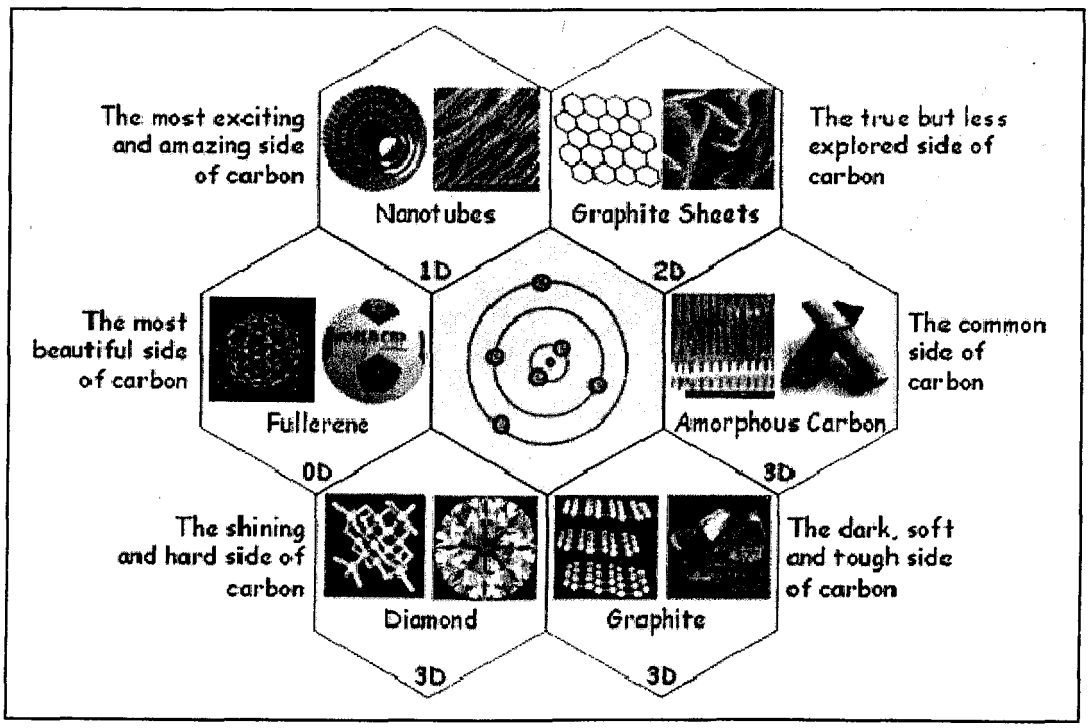

Figure 1.2. The allotropes of carbon family (Wu, 2009).

1.2.2 Carbon nanotubes

Carbon nanotubes (CNT), the focus of this study, have a nanometer-scale hollow tubular structure. While the diameter of a CNT is in the order of a few nanometers, their length can be in the order of several micrometers. There are two major types of CNT, namely single-walled carbon nanotubes (SWCNT), which consist of one tube of graphite, and multi-walled carbon nanotubes (MWCNT), which consist of a number of concentric tubes, cylinders inside the other cylinders. The diameter of SWCNT is very small (typically ~1nm), while the outer diameter of MWCNT ranges from 2.5 to 30nm (Harris, 1999). Nevertheless, the largest outermost tube in a MWCNT was found to be hundreds of nm (Meyyappan, 2005). CNT are basically rolled sheets of graphite, and for MWCNT, the interlayer spacing is approximately 3.4Å (Terrones *et al.*, 1997). Its body contains hexagonal rings and end cap with certain number of pentagonal rings, as illustrated in Figure 1.3.

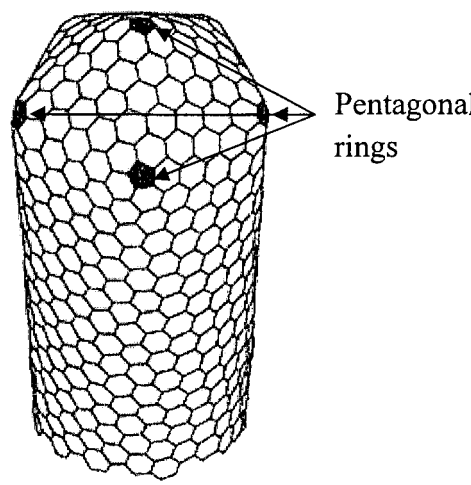

Figure 1.3. Structural model of a carbon nanotube (CNT) with a capped tip (Saito, 2004).

It is noteworthy that the electronic structure of individual SWCNT can be calculated. According to the calculations, SWCNT might be metallic or semiconducting depending upon their chirality (helicity) and diameter (Saito *et al.*, 1992b; Saito *et al.*, 1992a; Terrones, 2003). Depending on the direction of hexagons, nanotubes can be classified as either zigzag, armchair or chiral nanotubes, as illustrated in Figure 1.4. Different configurations of nanotubes have different electronic properties, either metallic or semiconducting.

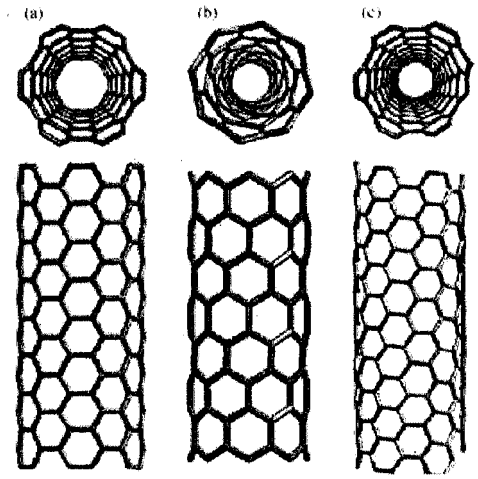

Figure 1.4. CNT presented at (a) armchair, (b) zigzag and (c) chiral configuration (MRSEC, 2010)

1.3 Natural gas and methane

Natural gas is a combustible gaseous fossil fuel, often found in underground reservoirs and comprised of methane and other hydrocarbon compounds. It attracts less attention compared to petroleum. But in recent year, it has been marked as the dawning of natural gas era and regarded as the fuel of the future (Krauss, 2010). Table 1.1 shows the composition of typical natural gas and natural gas found in

Malaysia reservoir. From the table, one can see that methane is the major component of natural gas. This simplest form of hydrocarbon is odorless, colorless and flammable gas with the chemical formula CH_4.

According to the Energy Information Administration (EIA) 2009 report, Malaysia held 83 trillion ft^3 of proven natural gas reserves as of January 2009 (EIA, 2009). Therefore, various routes for effective utilization of natural gas have been considered for its conversion to value-added product, such as the production of carbon nanofibers (CNFs) and CNT by methane decomposition. It is worth mentioning that methane decomposition not only produces CNFs or CNT, but also produces CO_x- free hydrogen as side product which can be utilized in proton-exchange membrane (PEM) fuel cells, oil refineries and methanol production.

Table 1.1. Composition of natural gas (NaturalGas, 2007; GasMalaysia, 2009).

Components		Typical	Malaysia
Methane	CH_4	70-90%	92.73%
Ethane	C_2H_6	0-20%	4.07%
Propane	C_3H_8		0.77%
Butane	C_4H_{10}		0.14%
Carbon dioxide	CO_2	0-8%	1.83%
Oxygen	O_2	0-0.2%	N.A.
Nitrogen	N_2	0-5%	0.45%
Hydrogen sulphite	H_2S	0-5%	N.A.
Rare gases	Ar, He, Ne, Xe	Trace	N.A.
Other hydrocarbon	-	N.A.	0.01

1.4 Hydrogen

Hydrogen is the lightest element on the periodic table with atomic number 1. It is extensively used in the petroleum and chemical industries. In a petrochemical plant, hydrogen is used for hydrodealkylation, hydrodesulfurization, and hydrocracking for refining of crude oil for wider use. In the food industry, hydrogen is used to hydrogenate oils or fats, which permits the production of margarine from liquid vegetable oil. Hydrogen is used to produce methanol and hydrochloric acid, as well as being used as a reducing agent for metal ores. More recently, using hydrogen as a clean fuel has been discussed. It is because when hydrogen is combusted, heat and water are the only products. Therefore, the use of hydrogen as fuel can greatly reduce green house gas emissions.

Future shortage of petroleum supply and solid fuels, such as coal and biomass, coupled with the increasing awareness of green house gas emissions increase the shift towards the alternative fuels sector. Hydrogen, in particular, driven by the penetration of efficient end-use technologies, is expected to increase its share dramatically, accounting for approximately 49 percent of the global final consumption by the end of the 21st century, and becomes the main final energy carrier (Barreto *et al.*, 2003).

1.5 Problem Statement

After nearly two decades from the discovery of CNT using various technologies, significant progress in their synthesis and applications has been demonstrated. Common methods employed for the production of CNT are the arc-discharge, laser ablation and catalytic chemical vapor deposition (CCVD). Among

these methods, CCVD method seems to be the most attractive method, given the potentiality for large scale production of CNT. By altering the operation parameters of CCVD process, the types and morphology of CNT such as MWCNT, SWCNT, Y-junction CNT, specific diameter, etc. can be controlled through tailor-made catalyst and increases the CNT yield by optimizing the process conditions.

On the other hand, the demand of hydrogen is expected to increase due to the increased utilization of proton exchange membrane (PEM) fuel cells as an alternative to internal combustion engines. To date, production of hydrogen is primarily achieved via steam reforming, partial oxidation, and auto thermal reforming of natural gas or stream reforming of methanol (Chin et al., 2006). However, CO is formed as by-product in these processes and must be subsequent removed. Moreover, the energy requirement for these processes is relatively high compared to catalytic decomposition of hydrocarbon (Ammendola et al., 2009). Therefore, decomposition of methane via CCVD method is currently being studied and has been proposed as an alternative route for the production of CO_x-free hydrogen. At the same time, the process involves the production of a very valuable product, which is CNT.

In previous work, an efficient catalyst, i.e. CoO_x-MoO_x/Al_2O_3 and the process for the production of CNT in a vertical reactor were developed (Chai, 2008). The CNT produced in the laboratory are same quality as the commercial CNT products produced by the companies in USA and UK (50-80% CNT, the remainder being amorphous carbon and residual metal catalysts) (NanoLab, 2010). Nonetheless, there are a few problems need to be overcome before the commercialization of CNT can be realistic. One of the restrictions is the amount of CNT produced for each run is very limited, due to the limitation caused by the use of vertical reactor. Only a small

amount of catalyst was used to avoid pressure buildup when synthesizing CNT, hence producing a very small amount of CNT. In this regard, it is of necessity to overcome this issue in order to obtain higher amount of CNT.

In the present research work, the use of horizontal reactor for the co-production of CNT and CO_x-free hydrogen was proposed. In a vertical reactor, a sudden pressure buildup in the reactor is often occurred, especially when a large amount of catalyst is used. It is due to the growth of CNT clogging the flow of gases through the catalyst bed. On the contrary, this problem is very unlikely to happen in a horizontal reactor. Other than that, more catalyst can be loaded and therefore it is expected more CNT will be produced per batch. Another advantage of horizontal reactor is the ease to set up and operate, which makes horizontal reactor easier to scale up for larger production. Optimization study of the synthesis of CNT in a horizontal reactor was carried out too in order to maximize the yield of CNT and with satisfying quality.

The rapid deactivation of catalyst is another common problem often encountered by researchers in the production of CNT by catalytic decomposition of hydrocarbons. In a CCVD process, hydrocarbons are catalytic decomposed, and the active sites of the catalyst are gradually covered by amorphous carbon, resulting the deactivation of catalyst. In this regard, the low life span of the catalytic activity has been the bottleneck preventing large scale production of CNT. In order to enhance the catalytic activity and to increase the sustainability of the catalyst, a weak oxidizer was suggested to remove the amorphous carbon covered on the active sites, thus prolonging the catalytic activity. Water vapor is a suitable weak oxidizer, as reported by Hata and coworkers (Hata et al., 2004). In the present study, the role of water vapor in enhancing the catalytic activity and lifetime was studied.

Since the discovery of CNT in 1991, the decomposition of high purity hydrocarbon, e.g. methane, ethylene, acetylene, etc, for CNT production is well reported in the past decades. However, these high purity carbon sources are costly and the supply is limited. On the other hand, low cost carbon sources such as natural gas and liquefied petroleum gas are present abundantly in Malaysia. In this regard, the possibility of replacing high purity carbon source by natural gas as the carbon source in CNT production was studied.

After summarizing the problems encountered in the synthesis of CNT, an optimization study on the production of CNT in a horizontal reactor was conducted, followed by the investigation of the role of water vapor in enhancing the catalytic activity and prolonging its lifetime for the production of CNT. Lastly, the decomposition of natural gas for the co-production of CNT and hydrogen was demonstrated.

1.6 Objectives

The present study has the following objectives:

1. To study the effects of reaction parameters on carbon yield and characteristic of produced CNT, and to determine the decisive process variables on production of CNT over CoO_x-MoO_x/Al_2O_3 catalyst in a horizontal quartz tube reactor. This is followed by optimizing the decisive process variables using response surface methodology (RSM) coupled with Box-Behnken design.

2. To evaluate the activity and lifetime of CoO_x-MoO_x/Al_2O_3 catalyst in water assisted methane decomposition, including the effect of water vapor

concentration and timing of water vapor introduction on the morphology of as-grown CNT.

3. To examine the decomposition of natural gas over CoO_x-MoO_x/Al_2O_3 catalyst at optimum condition for co-production of CNT and hydrogen.

4. To investigate the structural and morphology of as-produced CNT by performing various characterization on produced CNT.

1.7 Scope of the Study

This research study consists of three major sections; (i) process study of methane decomposition over CoO_x-MoO_x/Al_2O_3 catalyst, and then followed by optimization study of decisive parameters affecting the carbon yield and characteristic of the as-produced CNT in a horizontal reactor; (ii) investigation on the role of water vapor in enhancing catalytic activity and lengthening catalyst lifetime, as well as its effect on carbon yield and morphology of as-grown CNT; and (iii) utilization of natural gas as the carbon source for the production of CNT. The effluent gases are analyzed using an online-gas chromatograph (online-GC), and the CNT produced are characterized in order to determine the carbon yield and morphology of the CNT grown. These samples are characterized using thermal gravimetric analyzer (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and Raman spectroscopy.

Firstly, a preliminary study is conducted to examine the suitability of a horizontal quartz tube reactor for methane decomposition. Initially, the preliminary

study is conducted without catalyst, followed by the catalytic decomposition of methane over CoO_x-MoO_x/Al_2O_3 catalyst. This is to determine the capability of CoO_x-MoO_x/Al_2O_3 catalyst to decompose methane in a horizontal quartz tube reactor and to ensure the reactor material will not decompose methane at the reaction temperature.

Next, reaction process study is carried out to study the synthesis of CNT via catalytic decomposition of methane in a wide range of operating conditions; reaction temperature, reaction time, catalyst weight, metal loading, methane and nitrogen flow rates. The effect of these process parameters on the yield and quality of as-produced CNT are studied to determine the process variables that are significantly influencing the said responses. The determined decisive variables are then optimized to achieve high carbon yield with satisfactory characteristic. The process optimization is carried out using RSM coupled with Box-Behnken design. In the present study, the process optimization is performed with the aid of Design Expert v6.0.6. software.

Then, the research work is followed by investigating the role of water vapor in improving the catalytic activity and extending the catalyst span life. The effect of water vapor concentration, as well as the timing of water vapor introduction, on carbon yield and morphology of CNT produced is studied. Methane conversion is calculated based on the analysis of effluent gas by an online-GC, which is used to reflect the catalytic activity. Lastly, the decomposition of natural gas at the optimum condition is conducted to examine its competency in replacing high purity carbon sources for the production of CNT.

1.8 Organization of the Thesis

This thesis consists of five chapters. Chapter One (Introduction) gives an outline of the overall research project covering brief definition of nanotechnology and CNT. Information of natural gas and methane used as feedstock and hydrogen as by-product in this study are given as well. Problem statement is then defined after reviewing the existing limitations faced in the synthesis of CNT. Hence, this stresses on the need of this research project to overcome the limitations. The objectives of this research project are carefully set with the aim to solve the problems faced. Next the scope of this study is given. Finally, the organization of the thesis highlights the content and arrangement of each chapter.

Chapter Two (Literature Review) summarizes the past research works in the area of this research. This chapter starts with a brief discussion on common CNT synthesis methods, followed by a highlight on the synthesis of CNT via CCVD method, including process variables and their influences on CNT yield, as well as CNT morphology. Then, reactor configurations commonly employed for hydrocarbon decomposition are reviewed, aiming to report the feasibility and advantages of using horizontal reactor for the production of CNT. After that, a short review on design of experiment is given to identify the suitable types of statistical method and model for this research project. Finally, this chapter ends with a discussion on water assisted CCVD.

Chapter Three (Materials and Methods) discusses the experimental materials and the research methodology conducted in the present study. This chapter describes detailed information on the overall flow of this research work and also experimental methods used in conducting this research project. Besides, detailed information on

the materials and chemicals used in this study is also given. Finally, the analytical techniques and the conditions set for the equipment used for various characterizations for CNT are presented.

Chapter Four (Results and Discussion) is the most important chapter of the thesis. It encompasses detailed discussion on the findings obtained in this study. The main topics in this chapter include a preliminary study, process analysis of CNT formation in a horizontal reactor, followed by optimization study for CNT production via methane CCVD to obtain maximum carbon yield and CNT with satisfying characteristics. The effect of water vapor in methane decomposition is discussed afterward. Finally, the decomposition of natural gas over CoO_x-MoO_x/Al_2O_3 catalyst is demonstrated.

Chapter Five (Conclusions and Recommendations) summarizes the results obtained in this research study. This chapter concludes the overall research findings, and some concluding remarks are also made. Then, suggestions to improve the present studies are made and possible future studies to be conducted are being proposed. These recommendations and suggestions are given after considering the significant findings, the conclusions obtained as well as the limitations and difficulties encountered in the present work.

CHAPTER TWO:

LITERATURE REVIEW

This chapter reviews the studies reported in the literature related to this research project. A brief introduction of the common synthesis methods for the production of carbon nanotube (CNT) is delivered in the beginning of this chapter. The production of CNT via catalytic chemical vapor deposition (CCVD) method and the effects of process variables on the as-produced CNT are further reviewed and deliberated. Additionally, review on the employment of statistical design of experiment in process optimization is reported. Finally, this chapter ends with the discussion on water assisted production of CNT by CCVD of hydrocarbon.

2.1 Synthesis methods of carbon nanotubes

Ever since the discovery of CNT in 1991, its synthesis methods have gone through a significant evolution. The importance and extraordinary properties possessed by CNT have motivated many scientists to develop and improve the synthesis methods. In general, three major methods are well developed in synthesizing CNT. These methods, namely electric arc discharge, laser ablation and catalytic chemical vapor deposition (CCVD), will be further discussed in this section.

2.1.1 Electric arc discharge method

The electric arc discharge (EAD) is the first method used to produce CNT. EAD method is initially used to synthesize fullerenes (Iijima, 1991). The schematic diagram of EAD for CNT production is shown in Figure 2.1. In this method, two

graphite electrodes are connected to a power supply, and place linearly with the two ends are separated by a short distance (1-4mm) inside a low pressure chamber (50-70 mbar). A very high temperature (2000-3000°C) is obtained under an inert atmosphere of helium or argon, which allows the sublimation of the carbon from the positive electrode (anode) and deposition on the negative electrode (cathode). As a result, the length of the anode decreases as the CNT start forming on the cathode (Yakobson and Smalley, 1997; Journet *et al.*, 1997; Ebbesen and Ajayan, 1992; Poole and Owens, 2003; Dervishi *et al.*, 2009).

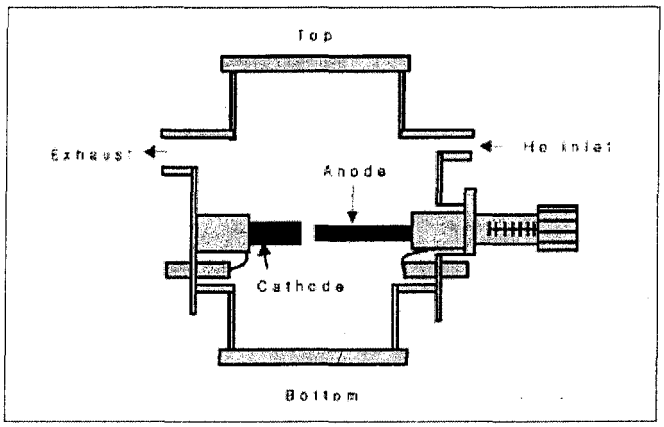

Figure 2.1. Schematic reactor setup for electric arc discharge (Nanodevice-Laboratory, 2010)

Two types of synthesis can be performed in the arc: evaporation of pure graphite (for the production of MWCNT) and co-evaporation of graphite and metal (for the production of SWCNT) (Paradise and Goswami, 2007). The first successful production of MWCNT at the gram level was developed by Ebbesen and Ajayan (1992). The purity and yield depend sensitively on the gas pressure in the reaction vessel (Ebbesen and Ajayan, 1992). In addition, MWCNT produced by the EAD method have fewer structural defects and better electrical, thermal, and mechanical

properties. Meanwhile, for SWCNT to be grown by EAD method, metal nanoparticles such as Fe, Co, Ni or their bimetallic catalyst, are needed to be embedded into the carbon anode (Bethune *et al.*, 1993; Iijima and Ichihashi, 1993). The catalyst plays a role in inducing the growth of SWCNT. Bethune and coworkers (1993) were the first who successfully synthesized substantial amount of SWCNT with the process parameters involved small gaps between electrodes, high current (100A), plasma between the electrode at about 4000K, voltage range (30-35V) under specified electrode dimensions. The EAD technique for CNT production seems simple, but it is difficult to obtain high yields of nanotubes and requires careful control of reaction conditions (Meyyappan, 2005).

2.1.2 Laser ablation method

In 1995, Smalley and his coworkers at Rice University introduced a very promising approach to produce CNT, called the laser ablation method (Guo *et al.*, 1995b). Laser ablation method is very similar to EAD method whereby the graphite rod is vaporized at high temperature and the vapor carbon condensed to form CNT. Figure 2.2 shows a schematic of laser ablation reactor setup. In laser ablation method, intense laser pulses are used to ablate a carbon target in a hot helium or argon atmosphere. As the graphite target inside a furnace is heated up at about 1200°C, a pulsed laser beam incident on the target starts evaporating carbon from the graphite. The carbon atoms from high temperature zone are then sweep by carrier gas to a cold copper collector on which they condense into CNT (Terrones, 2003).

Laser ablation method is a very efficient method for the production of SWCNT (Thess *et al.*, 1996). Regrettably, it is an extremely expensive technique as

it occupies high-purity graphite rods and high-power laser (Terrones, 2003). Similar to EAD method, transition metal catalysts are required in order to synthesize SWCNT. It is experimentally found that the SWCNT growth time in this technique is only last for a few milliseconds (Yudasaka *et al.*, 1999a; Zhang and Iijima, 1999; Sen *et al.*, 2000). Generally, this method can be used to produce long bundles SWCNT (Saito *et al.*, 1992a) and closed-ended MWCNT (Guo *et al.*, 1995a), and by-product such as fullerenes, amorphous carbon and other carbon by-product are produced.

The morphology and properties of CNT are highly influenced by the reaction parameters such as reaction temperature, type of hydrocarbon and carrier gas, light intensity and pressure (Dervishi *et al.*, 2009). For instance, no CNT are formed when the furnace temperature is below 800°C, whereas a maximum SWCNT yield is observed when the furnace is heated to about 1200°C (Yudasaka *et al.*, 1999b; Puretzky *et al.*, 2000).

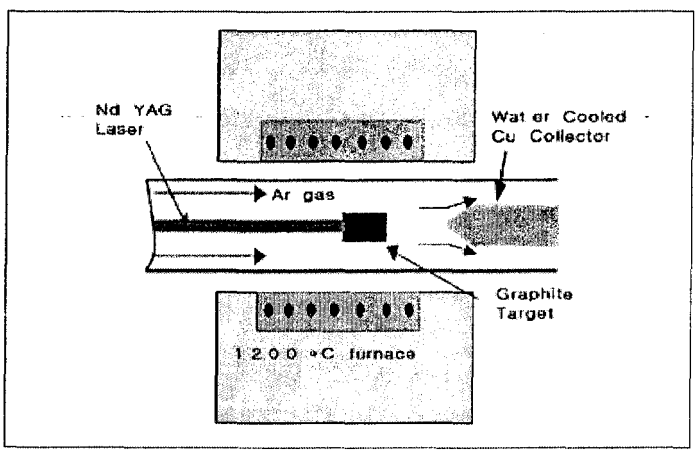

Figure 2.2. Schematic reactor setup for laser ablation method (Nanodevice-Laboratory, 2010).

2.1.3 Catalytic chemical vapor deposition method

Catalytic chemical vapor decomposition (CCVD) method enables the growth of CNT at low temperatures (<1000°C) from carbon-containing compounds which are decomposed catalytically on transition metal catalyst. The word catalytic is used to emphasize the role of metallic particles functioning as the nucleation sites for the CNT growth (Loiseau *et al.*, 2006). The formation of filamentous carbon by CCVD in industrial chemical processes such as steam reforming has been intensively studied for the past 50 years since the introduction of the transmission electron microscopy (TEM). Nevertheless, the CCVD growth of CNT was first introduced by Yacaman and coworkers in 1993 (José-Yacamán *et al.*, 1993).

CNT synthesized via CCVD method is essentially a two-step process, consisting of a catalyst preparation step followed by the growth of CNT. Common catalysts used are transition metal such as Ni, Fe or Co. The growth process involves heating of catalyst to high temperatures in a furnace and flowing of carbon-containing gaseous (usually hydrocarbon) through the tube reactor for a period of time. Once the hydrocarbon is decomposed into carbon and hydrogen, carbon atoms dissolve and diffuse into the metal surfaces and rearrange themselves into a network containing hexagons of carbon atoms and finally precipitate out in the form of CNT (Öncel and Yürüm, 2006; Dervishi *et al.*, 2009). The catalyst could be deactivated when all the metal surfaces are covered by amorphous carbon or encapsulated by CNT, and thus hydrocarbon gases no longer come into contact with the active sites, which result in the cessation of CNT growth (Yamada *et al.*, 2008).

It is worth mentioning that the excellent versatility possessed by CCVD enables the utilization of hydrocarbons in any state (solid, liquid or gas) to synthesize CNT. The hydrocarbon source exploited in the CVD method can be in a gaseous state such as acetylene, methane, and ethylene, a liquid state such as benzene, alcohol, and hexane, or a solid state such as camphor and naphthalene. Hydrocarbon in the gaseous form can be purged directly into the reaction furnace, while hydrocarbons in liquid and solid forms require preheating before entering the reactor. (Terranova *et al.*, 2006; Dervishi *et al.*, 2009). Figure 2.3 shows a schematic diagram of the CCVD method exploiting the carbon source in any state, i.e. gas, liquid and solid.

CCVD is marked as the most favorable synthesis method because it is a simple and low cost process, yet able to synthesize CNT in high yield, not to mention can be easily scaled-up to industrial production (Daenen *et al.*, 2003). Furthermore, CCVD method is ideally suited to synthesize CNT for advanced applications in the fields of electronics and optoelectronics, or when a specific CNT architecture is required (Teo et al., 2005). In the present work, CCVD method is employed to produce CNT. In view of this, the production of CNT via CCVD method is discussed in depth in next section.

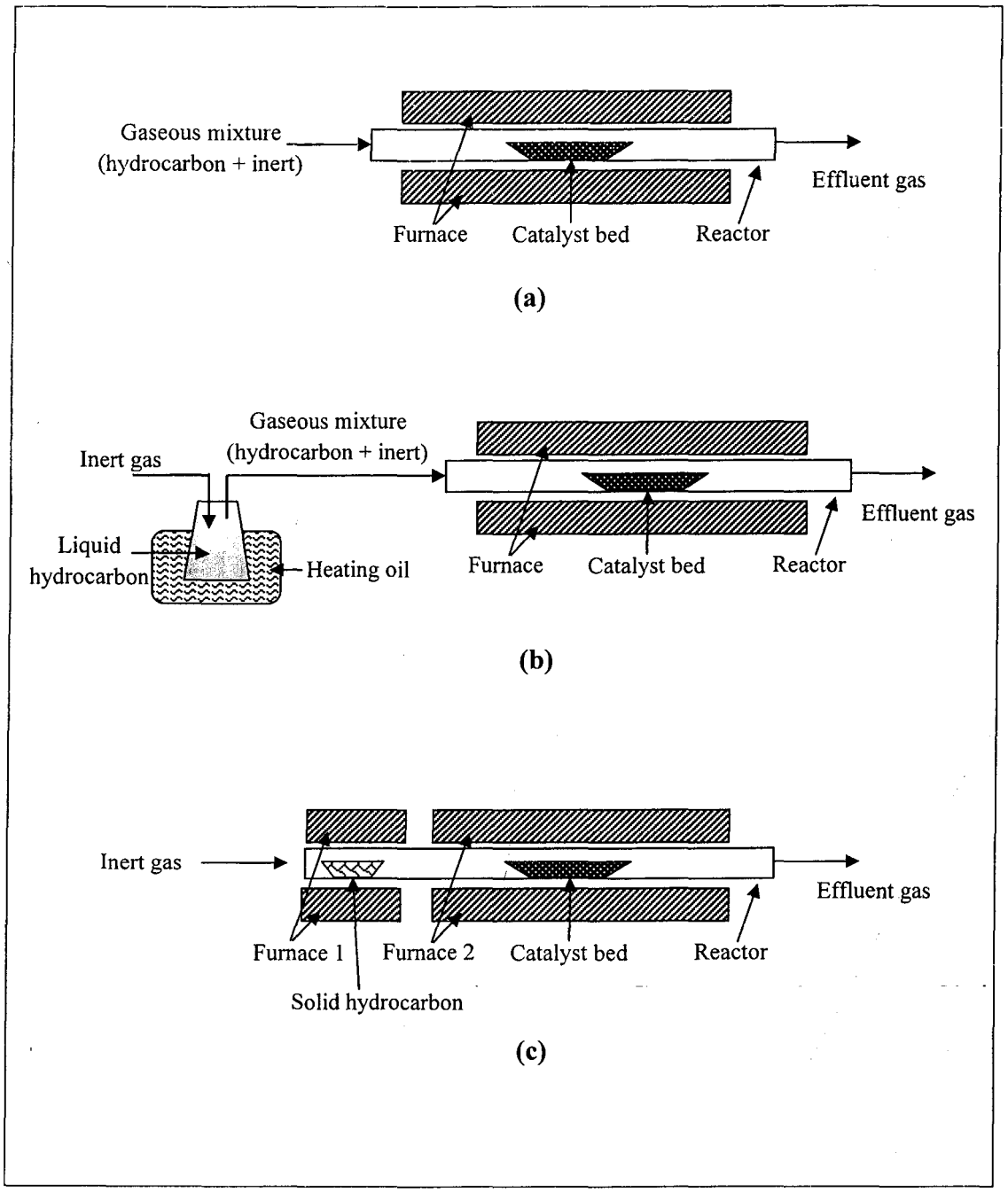

Figure 2.3. Schematic diagram of a CCVD setups utilizing three different types of hydrocarbons: (a) gas, (b) liquid and (c) solid.

2.2 Synthesis of carbon nanotubes via catalytic chemical vapor deposition method

Compared to other CNT growth techniques, catalytic chemical vapor deposition (CCVD) has been regarded as the most promising method for large scale production of CNT due to its advantages of low cost, high yield, mild operating conditions and easily control (Cheng *et al.*, 1998). In the CCVD process, the production of CNT can be controlled by varying the reaction parameters such as type of catalyst used, reaction temperature, and flow rate of feedstock (Shajahan *et al.*, 2004). These tunable parameters affect the types of carbonaceous material grown, the quality and quantity of the as-produced CNT. This section reviews the important variables that need to be considered in synthesizing CNT via CCVD method, such as type of catalyst, metal loading, reaction temperature, carbon feedstock and gas hourly space velocity (GHSV).

2.2.1 Catalyst

Catalyst is the heart of the CCVD synthesis of CNT and therefore developing an adequate catalyst is crucial to obtain the desired CNT morphology as well as production yield. Hence, careful selection of the catalyst is of importance in the CCVD synthesis. It is well accepted that transition metals such as Ni, Fe or Co in the form of nanoparticles are considered as the most effective catalysts. However, the doubt is which catalyst is more effective and active to provide CNT with better quality as well as yield. Supported nickel has been identified as the most effective catalyst for methane decomposition, thus nickel-based catalysts are frequently being employed for industrial use (Zhang and Amiridis, 1998; Li *et al.*, 2006b; Konieczny

et al., 2008; Ashok *et al.*, 2009). Meanwhile, iron supported on alumina was very efficient at the temperature range of 600-650°C (Reshetenko *et al.*, 2004; Alexiadis and Verykios, 2009). The effect of selected catalyst (Ni, Fe and Co) on the synthesis of CNT studied by Lee and coworkers revealed that the growth rate of CNT is in the order of Ni> Co> Fe (Lee *et al.*, 2002). Noble metal such as rhodium, ruthenium and platinum have been proposed as active metals in hydrocarbon decomposition into CNT (Otsuka *et al.*, 2000; Ichi-oka *et al.*, 2007). Ichi-oka *et al.*(2007) claimed that aforementioned noble metals supported on MgO gave higher yield of carbon than cobalt, iron and nickel from decomposition of methane. However, the use of noble metals is not feasible from the economic point of view.

In order to enhance the performance and catalytic activity of the catalyst, a promoter can be added to the catalyst. A promoter is a component of catalyst system which does not involve directly in the chemical reaction like active metal does, but it helps to enhance the performance and activity of solid catalyst (Chai *et al.*, 2009b). Possible promoters being used include Mn, Mo, Ni, Cu and Pd (Alvarez *et al.*, 2001; Lamouroux *et al.*, 2007; Ashok *et al.*, 2009; Chai *et al.*, 2009b; Chesnokov and Chichkan, 2009; Landois *et al.*, 2009; González *et al.*, 2010; O'Byrne *et al.*, 2010; Zoican Loebick *et al.*, 2009). A proper choice of promoter will greatly improve the carbon yield and the morphology of CNT formed as well as prolong the catalytic activity of the catalyst for the growth of CNT, which are lacking in monometallic catalyst (Avdeeva *et al.*, 1996; Alvarez *et al.*, 2001; Kathyayini *et al.*, 2004; Reshetenko *et al.*, 2004; Ashok *et al.*, 2009). Avdeeva et al. (1996) reported that by adding Cu on the catalyst as promoter, up to 250 g/g_{cat} of filamentous carbon was produced by methane decomposition. The adding of promoter can affect the morphology of as-produced CNT too. For instance, an addition of a small amount of